

Ground state energy, electronic and chemical properties: An investigation of linear acenes (n=1 to 7) linked Thiophene for Organic electronic material

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Abstract

We report a theoretical study of linear acene (n=1 to 7) linked thiophene functionality. The total ground state energies, HOMO-LUMO energy gap, frontier orbitals energies, electron affinity and ionization potential are calculated at DFT-B3LYP/6-311G* and MP2/6-311G* exchange level of the theory and basis set. The results show a good agreement when compared with the theoretical and experimental values. It is found that total ground energy of the system, HOMO-LUMO gaps energy, electrophilicity, electronegativity and chemical hardness decrease with the increasing number of electrons or acenes ring. The global chemical indices; electronegativity (χ), electrophilicity (ω) and chemical hardness (η) is observed to decrease as the number of electrons in acenes ring increase, whereas softness (S) and chemical potential (μ) increases with the increasing number of electrons around molecules. Also, the frontier orbital energies, Ionization energies, and electron affinity results show an improvement as compared to the acenes molecules.

Keywords. Frontier orbitals; Chemical potential; global hardness; HOMO-LUMO energy

Introduction

Interest in the research of π -conjugate organic semiconductor materials has potentially increased over a decade in materials science, chemistry as well as space physics. They display promising advantages over a traditional inorganic material such as lower cost production, light weight, flexibility, large coverage area [1], low temperature and soluble-based processes [2], and they also possess good promising mechanical properties [3]. The π -conjugate organic semiconductor materials demonstrate great important applications in light emitting diode (OLED), energy storage, photovoltaic cells, organic thin film transistors (OTFT), electrochromic devices, sensors [4], electronic paper and flat panel liquid crystal displays [5] and organic electrochemical transistor as biocompatible for brain-machine interface [6].

Although, despite the merit displayed by organic semiconductor material, there is a setback among organic materials for device application such as intrinsic instability of radical ions in the air, poor solubility and high barrier for electron injection for electrode work function that uses noble metals, which are sensitive to light, oxygen, and polymerization [7, 8]. However, there is some literatures addressed to improve the instability in the air, charge mobility and charge enhancement [9] [10-12]. This work examines the substitutional effect of thiophene on acenes organic semiconductor at a difference position of acene for the enhancement of electronic properties. The computation is carried out at DFT and MP2 level of the theory with B3LYP exchange and 6-311G* basis set. NWchem version 6.3 is used to predict the ground state molecular energies and electronic properties.

Methods

The Density Functional Theory, B3LYP exchange level and MP2 theory are employed for the computation. The molecules properties are optimized and calculated at B3LYP/6-311G* and MP2/6-311G* exchange level and basis set with NWchem version 6.3 [13, 14]. Molden is used for visualizing interface [15]. The total ground state energies and frontier orbital (HOMO and LUMO) energies, HOMO-LUMO energy gap, E_{gap} are presented here.

Results and Discussion

The calculated ground state energy, (GSE) is given in Table1, which is compared with the theoretical and experimental results. Figure 1 shows the variation of total ground state and HOMO/LUMO energy as a result of the introduction of thiophene molecule to the acenes. The results reveal a linear dependency on the number of electrons or acene ring. The increase in frontier orbital energies tends to change the electronic and chemical properties of linear acene. Figure 2 displays a decrease in the ground state energy as the number of electrons or rings increase, and confers the result with other theoretical and experimental data.

Table 1. Ground state energy, Frontier orbitals (HOMO and LUMO) energy

n	Molecules	DFT-B3LYP/6-311G*	MP2/6-311G*	DFT-B3LYP/6-311G*		MP2/6-311G*	
				HOMO	LUMO	HOMO	LUMO
1	M1	-1336.0665	-1333.2683	-6.2778	-0.9807	-6.2778	-0.9807
2	M2	-1489.7475	-1486.4862	-6.0270	-1.6653	-6.0270	-1.6653
3	M3	-1643.4243	-1639.6955	-5.5507	-2.3308	-5.5507	-2.3308
4	M4	-1797.1002	-1792.9002	-5.1388	-2.8336	-5.1388	-2.8336
5	M5	-1950.7729	-1958.1393	-4.8514	-3.2282	-4.8514	-3.2282
6	M6	-2104.4464	-2099.3039	-4.6259	-3.4930	-4.6259	-3.4930
7	M7	-2258.1196	-2252.5059	-4.4429	-3.6877	-4.4429	-3.6877

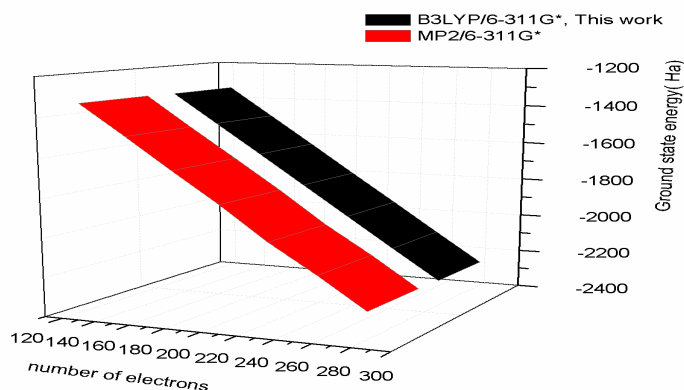


Figure 1 Total ground state energy variation to the number of electrons.

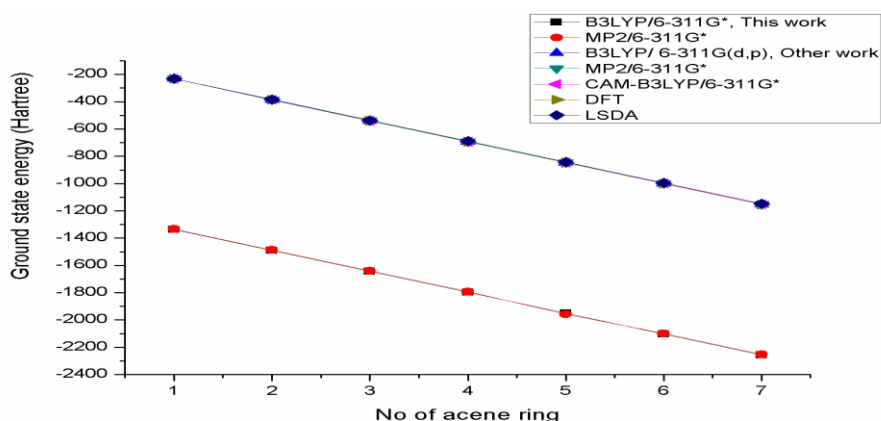


Figure 2 Total ground state energy variation conferred to other ^[16] theoretical results with the number of rings.

However, in Figure 3 (a) there is a linear increase in the Coulomb potential and nuclear repulsion energy as the amount of electrons increase. Thus, possibly, the graph illustrates the approximation in Quantum mechanics method, a Born-Oppenheimer approximation, which neglects the motion of the nucleus [17]. And at a ground state energy level in Figure 3 (b), potential energy and nuclear repulsion were decreasing with an increase of the acenes ring.

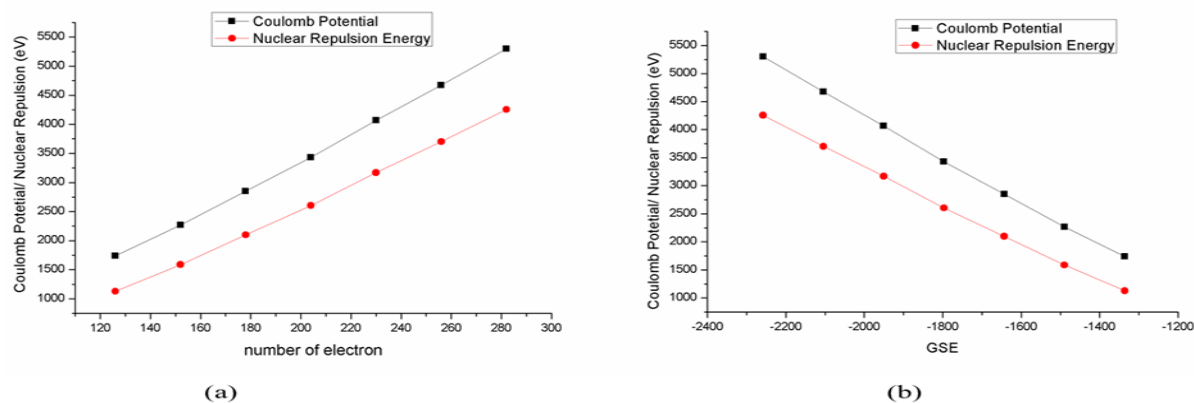


Figure 3 (a) and (b).Coulomb potential and nuclear repulsion energy plotted against the number of electrons and GSE, unit (Hartree)

Conclusion

The total ground state, electronic properties of the predicted linear acenes ($n=1$ to 7) linked thiophene at DFT and MP2 are studied from a theoretical framework. The property is investigated as the function of increasing number of electrons of acenes ring. The increase of thiophene tends to change the properties of acene.

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